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## Modtaget

Process for the preparation of an elongated polymer  
article and a flexible unbonded offshore pipe

5 The present invention relates to a process for the  
preparation of an elongated article such as a tube-formed  
article. The invention particularly relates to a process  
for the preparation of a flexible unbonded offshore  
pipeline comprising a tube-formed polyethylene layer e.g.  
an inner liner. The invention also concerns a flexible  
10 unbonded offshore pipe comprising a polymer layer  
obtainable according to the process.

Flexible unbonded offshore pipes comprising a tube-formed  
inner liner and at least one reinforcement layer are  
15 generally used for the transportation of oil and gas  
products over long distances and often at elevated  
temperatures such as above 60 °C or more.

Offshore pipes are also used for injection of chemicals  
20 into a sub-sea drilled well e.g. connected between a host  
oil platform and a sub-sea satellite installation.

Offshore pipes must be capable of operating at high  
pressures, and the pipes should be resistant chemicals  
25 and water including seawater. Furthermore such offshore  
pipes should be flexible so that they can be spooled onto  
a drum or reel.

Offshore pipes are normally very long, so-called risers  
30 often several hundred meters long and so-called flow-  
lines often several kilometers long. They are laid on the  
seabed, typically subjected to high pressures and  
pressure differences along the pipeline. When the  
pipeline is transporting oil or gas, the pipelines may be  
35 exposed to temperatures substantially above 60°C. The

offshore pipes should therefore be capable of operating at high temperatures and high pressures.

Offshore pipes generally comprise one or more tube-formed barrier layers including an inner liner and at least one reinforcing layer. The inner liner is the barrier layer, which is exposed to a fluid, e.g. oil transported in the pipeline. In most situations, the pipeline also comprises an outer sheath providing a barrier to the outer environment such as seawater. The pipe normally comprises one or more reinforcing layers between the inner liner and the outer sheath, and some pipes also comprise a reinforcing layer inside the pipe, called a carcass. The carcass prevents collapse of the inner liner and provides mechanical protection to the inner liner. Some pipes also comprise one or more intermediate polymer layers.

The inner liner should be chemically stable and mechanically strong even when subjected to high temperatures. Furthermore, the inner liner should be manufactured in one piece since repair, welding or other types of connecting methods are not acceptable for inner liners in offshore pipelines. The inner liner is therefore normally produced by continuous extrusion of a polymer. A number of polymers are presently used for the production of inner liners, such as Polyamide-11 (PA-11), polyethylene (PE) and Polyvinylidene difluoride (PVDF).

These materials shall fulfil the combined requirements of e.g. heat stability, resistance to crude oil, seawater, gases, mechanical fatigue, ductility, strength, durability and processability. The inner liner material is normally selected on a case-to-case basis after careful investigation of the conditions for the planned installation. Here, cross-linked polyethylene may in many cases prove to fulfil the requirements.

Additionally, the interest for use of inner liners in corrosive applications with high concentrations of carbon dioxide and/or hydrogen sulphides is increasing. Furthermore, polyamides are susceptible to hydrolysis and aliphatic polyketones are also susceptible to degradation at elevated temperatures. However, the permeability of gases increases with temperature, and polyethylene has a relatively high permeability to gases. Thus permeation of gases like methane, carbon dioxide and hydrogen sulphide may in some cases be prohibitive for use of cross-linked polyethylene inner liners at high temperatures.

In EP 487 691 it has been suggested to use an inner liner of cross-linked polyethylene. An inner liner with such cross-linked material has shown to be highly improved compared to inner liners of the similar non-cross-linked (thermoplastic) material.

In order not to degrade the material, the process in the prior art of producing an inner liner is carried out in two steps, first the material in non-cross-linked form is manufactured by extrusion, and afterwards the material is cross-linked. When the material is cross-linked, it is only to some degree possible to change its shape without degrading the material.

The cross-linking step is often very cumbersome and time and space demanding. EP 487.691 describes the cross-linking step of silanized polyethylene with reference to the figures. The pipeline is first manufactured by extrusion of the inner layer of polyethylene, followed by metal armouring and outer sheathing. The entire multilayer pipe structure is mounted with end fittings, and the flexible pipe is connected to a device for circulating water in the inner liner tube. The water is

heated to about 92-98 °C and circulated using pumps. The time of cross-linking is between 48 and 120 hours followed by a step of cooling for about 20 hours.

5 By this process, it is necessary to manufacture the entire pipe before making the actual cross-linking of the inner liner. In case of a quality problem of the inner liner, it appears impractical to make the entire pipe without assuring final properties of the cross-linked  
10 inner liner. The patent describes both the use of a Sioplas® process involving peroxide-activated grafting of the vinylsilane onto the polyethylene in a separate compounding step, and the Monosil® process with in-situ silane grafting of polyethylene. It is preferred to use a  
15 dibutyltindilaurate (DBTDL) as cross-linking accelerator and a density of the polyethylene above 931 kg/m<sup>3</sup>, preferably over 940 kg/m<sup>3</sup>.

The required properties for the other polymer layers  
20 (intermediate layer(s) and outer layer are much similar to the required properties of the inner liner.

The object of the present invention is to provide an improved process for the preparation of an elongated  
25 article such as a tube-formed article by extrusion of a polyethylene polymer followed by cross-linking, which method does not have the drawbacks of the processes described above and which process in particular is faster and less space demanding than known processes.

30

A further object is to provide a process for the preparation of an elongated article having a length of at least 50 meters by extrusion of a polyethylene polymer followed by cross-linking, which method is faster and  
35 less space demanding than known processes.

Yet a further object of the invention is to provide a process for the preparation of a flexible unbonded offshore pipe comprising a tube-formed inner liner, which comprises extrusion of a polyethylene polymer inner liner  
5 followed by cross-linking, which method is faster and less space demanding than known processes.

These and other objects are achieved by the invention as defined in the claims.

10

The process of the present invention may in principle be used for the preparation of any type of elongated article of polyethylene-based polymers, such as any tube-formed article. However, the process of the invention is  
15 particularly useful for the preparation of flexible unbonded offshore pipes comprising tube-formed polymer layer(s), e.g. an inner liner, an intermediate polymer layer and/or a cover layer. The process is specifically useful for the manufacturing of so-called endless  
20 offshore pipes, i.e. pipelines having a length of 50 m or more.

The process for the preparation of an elongated polymer article according to the invention comprises the steps of  
25 shaping a polymer material by extrusion into or onto a supporting unit in an extrusion station and in a subsequent step cross-linking the extruded polymer material to obtain hardening and high strength of the material.

30

The polymer material comprises a polyethylene and an amount of peroxide for cross-linking of the polyethylene. The peroxide should have an activation temperature substantially above, preferably at least 5 °C above, and  
35 more preferably at least 10 °C above the temperature of the polymer material during the extrusion thereof. The

term "substantially above the temperature of the polymer material during the extrusion thereof" means that the peroxide should not be activated during the extrusion.

5 The peroxide is thus chosen to have an activation temperature above the temperature of the polymer material during extrusion to avoid that activated peroxide will induce cross-linking during extrusion. During extrusion, cross-linking of the polymer is highly undesired, as it  
10 will complicate the extrusion. In the process, the extrusion and the cross-linking steps are carried out in an in-line process, including passing the extruded polymer material directly through a cross-linking zone with heating means to activate the peroxide to obtain  
15 cross-linking. Thus, the cross-linking step is carried out in a separate step subsequent to the extrusion step.

The polymer material, which is shaped during the process, comprises polyethylene. In a preferred embodiment,  
20 polyethylene constitutes the major part of the polymer material, and only minor parts of other polymers are present. For some purposes, it is preferred that polyethylene is the only polymer material present.

25 Polyethylene is often used for inner liners for offshore flexible pipes at operational temperatures up to about 60°C. Primarily the high density polyethylene (HDPE), which has a substantially linear chain structure, is used. The HDPE has a somewhat higher stiffness and  
30 mechanical strength than other polyethylene types. Also, it has a higher crystallinity and therefore a lower permeability to gases. The typical HDPE used for inner liners are pipe grades with a density of 945 to 955 kg/m<sup>3</sup>, and preferably around 950 kg/m<sup>3</sup>. Preferred  
35 polyethylene to be used according to the invention has a density above 920 kg/m<sup>3</sup>, such as e.g. above 940 kg/m<sup>3</sup>

In general, it is preferred that the polymer composition comprises at least 50 % by weight, preferably at least 70 % by weight, more preferably at least 85 % by weight of polyethylene.

The polymer composition may include up to about 40 % by weight, such as up to about 20 % or preferably up to about 10 % by weight of additional polymer(s) other than polyethylene. The additional polymer(s) may e.g. be selected from the group consisting of thermoplastics such as thermoplastic elastomers including block copolymer such as SEBS, SBS, SIS, TPE-polyether-amide, TPE-polyether-ester, TPE-urethanes, TPE PP/NBR, TPE-PP/EPDM; TPE-vulcanisates and TPE-PP/IIR; rubbers such as butadiene rubber, isoprene rubber, nitril rubber, styrene-butadiene rubber and urethane rubber; polyolefins such as polypropylene and polybutylene including its isomers; liquid crystal polymers; polyesters; polyacrylates; polyethers; polyurethane; thermoplastic vulcanisates; and Liquid Silicone Rubber.

The polyethylene material typically contains minor amounts of additives like pigments, heat stabilisers, process stabilisers, metal deactivators, flame-retardants and/or reinforcement fillers. It is preferred to keep the amount of such additives low to reduce the risk of blistering and stress induced cracking. The reinforcement fillers may include carbon black, glass particles, glass fibres, mineral fibres, talcum, carbonates, mica, and silicates.

According to the invention the cross-linking of the polymer material is initiated by peroxide serving as a radical-former when activated. A specific peroxide decomposes at a specific temperature (the activation



temperature of the peroxide). The decomposition causes the peroxide to release radical-formers, which induce cross-linking in the polymer material. The temperature during the extrusion is typically between 145 to 200°C.

5 The temperature during extrusion is selected to keep the polymer material in a molten state. Cross-linking of the polymer is undesired during extrusion, as it will make the extrusion more difficult. Thus, it is preferred to select a peroxide having an activation temperature above

10 145°C or even above 150°C. Preferably the selected peroxide has an activation temperature which is substantially above (such as at least 1 °C), and preferably at least 5 to 10°C above the temperature of the polymer material during the extrusion. Consequently

15 it is preferred to select a peroxide with a higher activation temperature such as butylcumylperoxide, dicumylperoxide, Trigonox 145B or a hydroperoxide, e.g. butylhydroperoxide.

20 In general, the amount of peroxide in the polymer composition should preferably be at least 0.1 % by weight of the polymer composition, such as between 0.2 and 3 % by weight of the polymer, more preferably up to about 2 % or even more preferably up to about 1.5 % by weight of

25 the polymer composition.

To obtain a satisfactory cross-linking of the polymer material it is preferred that the polyethylene contains peroxide from 0.1 to 1.0 % by weight, and preferably from

30 0.3 to 0.8 % by weight.

According to the invention the extruded polymer material is passed to a cross-linking zone and activated using heat. The heat may in principle be applied using any

35 heating means which can supply sufficient heat for the activation. The object of the heating means is thus to

heat the extruded polymer material to a temperature sufficient to activate the peroxide in the polymer material. When the peroxide is activated, it will induce cross-linking in the polymer material as described above.

5 The heating means in the cross-linking zone are preferably infrared heaters, microwaves or conventional heaters such as electric wires, gas or oil-burners. The heating may also be by hot gas or hot gas with moisture, such as hot moistened air or hot steam. The moisture in  
10 the gas may provide a better transmission of heat than if the gas is a dry gas. The heating means in the cross-linking zone is preferably arranged in such a way that the polymer material is subjected to heat treatment from all sides or angles in the cross-linking zone. For  
15 instance when the polymer material has a circular cross section, the heating means are placed all around the circumference of the cross-section to obtain the best possible heating effect on the polymer material.

20 The time for performing the crosslinking in the cross-linking zone depends mainly on the thickness of the polymer layer, the type of peroxide used including its activating temperature, and the method used for applying heat in the cross-linking zone. In some applications, the  
25 cross-linking time may be relatively long, e.g. 10 minutes or even longer, but in order to optimize the in-line process and the space occupied by the cross-linking zone, the time for performing the cross-linking should preferably be adjusted to be about the time for extruding  
30 0.05 to 2 m, preferably 0.2 to 1 m of the polymer material. This adjustment may be performed by regulating the application of heat, the selection of type of peroxide, and the thickness of the extruded polymer. Also the extrusion velocity may be adjusted.

35

When the process according to the invention is a

preferred embodiment using infrared heaters or microwaves as heating means, the extruded material is subjected to a heat treatment in the cross-linking zone for 5 to 120 seconds, and preferably for 10 to 60 seconds.

5

In a preferred embodiment, the extruded polymer material is subjected to a heat treatment in the cross-linking zone at a temperature above 145°C and preferably at a temperature between 150 and 200°C to secure activation of the peroxide. The optimal temperature depends on the type of peroxide and can easily be found by a few experiments.

10

Compared with prior art techniques, the degree of cross-linking is high in the process according to the invention. The degree of cross-linking obtained is 75 to 90 %, and preferably the degree of cross-linking is 80 to 85 % according to ASTM D 2765. Thus, cross-linking appears in both the amorphous and crystalline phase of the polymer material.

15

20

In a preferred embodiment of the process according to the invention, the pressure in the cross-linking zone is raised above ambient pressure. By increasing the pressure in the cross-linking zone, formation of bubbles and irregularities in the polymer material can be avoided. The pressure is preferably raised to 1.5 bar above ambient pressure, more preferably 2 bar above ambient pressure, and typically the pressure in the cross-linking zone is between 2.5 and 10 bar.

25

30

In order to avoid undesired deformation or reactions in the extruded polymer material, it is preferred that the extruded polymer material enters the cross-linking zone immediately after extrusion or no later than 2 minutes after extrusion. By passing the extruded polymer material from the extruder to the cross-linking zone, the

35

temperature of the polymer material may be kept close to the extrusion temperature at the entrance to the cross-linking zone, which means that the necessary amount of energy for activating the peroxide is as low as possible.

5 Generally, it is preferred that the temperature of the polymer material at the entrance to the cross-linking zone is at least 100 °C, preferably at least 120 °C and even more preferably at least 140 °C. The entrance is defined as the place between the extruder and the cross-  
10 linking zone where the temperature of the polymer material is lowest.

Moreover, in order to optimise the properties of the extruded product and avoid deformation, it is preferred  
15 that the velocity of the extrusion of the polymer material is approximately equal to the velocity of the extruded polymer passing through the cross-linking zone, and the velocity is preferably between 0.2 to 2 m/minute, and more preferably between 0,5 and 1,0 m/minute.

20 Preferably the extruded polymer material from the cross-linking zone is cooled to ambient temperature, e.g. the polymer material may be cooled in a cooling zone with water or air.

25 The supporting unit may in principle be any kind of supporting means which supports the polymer material as it passes out from the extruder. The supporting unit onto which the polymer material may be extruded may simply be  
30 a mandrel, net or hollow wire. The supporting unit onto which the polymer material may be extruded may preferably be a tube-formed unit, such as a calibrating device (calibrator). Such calibrator is generally known from the art of extruding inner liners for flexible unbonded  
35 offshore pipes without inner reinforcing layer(s) (Carcass). A calibrator may e.g. calibrate the outer

dimension of the pipe or tube shaped polymer layer using vacuum suction onto a solid surface e.g. metal surface, which surface may preferably be wetted with water for lubricating.

5

Thus, in a preferred embodiment the polymer article is an inner liner of a flexible unbonded offshore pipe without carcass, and the inner liner is extruded into a supporting unit, preferably in the form of a calibrator.

10

In a preferred embodiment of the process according to the invention, the supporting unit is a reinforcement material, and preferably a reinforcement layer of a flexible unbonded offshore pipe.

15

The supporting unit may e.g. be in the form of a carcass, in which case the polymer article is an inner liner of a flexible unbonded offshore pipe and the polymer material is extruded onto the carcass to form the inner liner.

20

Where the polymer article is an intermediate layer of a flexible unbonded offshore pipe, the supporting unit may preferably be in the form of a pressure armour, and the polymer material is extruded onto the pressure armour.

25

Where the polymer article is an outer cover of a flexible unbonded offshore pipe, the supporting unit may preferably be in the form of a tensile armour, and the polymer material is extruded onto the tensile armour.

30

Please observe that the term "outer cover" does not exclude that further armouring layer or layers are applied around the outer cover, but in general this term should be interpreted to mean that the outer cover is the outermost pipe shaped polymeric layer.

35

Generally, it is preferred that the supporting unit

material is a metallic material, preferably shaped as a carcass, a pressure armour or a tensile amour of metallic material. The metallic material may preferably be capable of reflecting heat from the heating means in the cross-linking zone thereby increasing the effect of heating on the polymer material. This reflective effect will lead to faster and more effective activation of the peroxide and cross-linking of the polymer material.

When extruding a polymer layer onto a supporting unit in the form of a carcass or another amour, it is generally preferred that a tape or film layer is applied onto the amour prior to the application of the polymer layer. Thereby undesired deformation of the polymer layer due to the shape of the surface of the amour which may e.g. be made from profiles engaged into each other, may be avoided. In one embodiment, wherein the supporting unit is an amour layer and this layer comprises a tape applied onto the amour and the polymer composition is extruded onto this tape, it is preferred that the tape has a reflecting surface reflecting the heat applied in the cross-linking zone. The tape may e.g. comprise a metallized surface, e.g. Al metallized. The reflecting surface of the tape may preferably be capable of reflecting at least 50 % of the heat applied to the tape when using infrared heating or microwave heating.

Preferably the elongated polymer article obtained by the process according to the invention is an inner liner, preferably an inner liner for an offshore pipe.

The cumbersome and time-consuming cross-linking of the inner liner as well as the outer cover and/or intermediate layer or layers of a flexible pipe product, as described in EP 487.691, can be overcome by the present invention, in particular by initiating the cross-

linking in-line (or on-line) with the extrusion of the inner liner. By in-line is simply meant 'in the same continuous process step'. As a result the liner material completes the cross-linking within the cross-linking zone  
5 without any further treatment, and e.g. before the final multilayer pipe structure is completed.

By the present invention, cross-linking of the inner liner may be terminated prior to the making of the metal  
10 armouring and outer sheath and the end fittings. This is advantageous for several reasons. Quality control is made earlier in the production cycle and necessary corrections can be made earlier. Also, by the present invention it is possible to cut samples from the end of the cross-linked  
15 inner liner for measurements of the degree of cross-linking. It is not possible to do so on a finished pipe. If this should be done on a pipe according to the EP 487.691, it would require cutting off a section of the pipe and establishing a new end fitting, which is costly  
20 and time consuming.

In one embodiment according to the process of the invention, polyethylene and other ingredients for the polymer composition including the peroxide and  
25 accelerator may be melted and homogenised in an extruder, which feeds the polymer melt into a distributor and a tool, either a crosshead tool or a pipe tool. With a crosshead tool, a metal carcass may be fed into the centre of the crosshead tool, and the polymer may be  
30 extruded around this metal cylinder. The carcass may be at ambient temperature (cold) or preheated to avoid rapid quenching of the polymer melt. The inner liner thickness may typically be 4 to 10 mm when using a carcass, and somewhat larger, typically 6 to 16 mm without a carcass.

35

After extrusion of the pipe, using a crosshead tool, into which the carcass is fed, the polymer melt forms a cylindrical object around the carcass.

- 5 Alternatively, the inner liner may be made without a metallic carcass e.g. using pipe tool (or a crosshead tool), and in this case the extruded object may pass through a calibrator as described above.
- 10 After cooling, the pipe passes out of the cooling chamber and is dried, typically by a wipe-off device and blowing with air. Then a drawing device, typically a caterpillar device, draws the pipe forward. It is important that the polymer inner liner here is cooled below the softening
- 15 point, as the caterpillar belts will otherwise cause mechanical damage to the inner liner. After the caterpillar, the pipe is spooled on a drum, reel or turntable. The metal armouring and the subsequent extrusion of the outer sheath are normally performed in
- 20 separate steps.

After the extrusion, the extruded polymer tube is passed into a cross-linking zone as described. An example of an in-line cross-linking equipment is outlined in Figure 1

25 and described below.

The invention also relates a method for the production of a flexible unbonded offshore pipe comprising one or more polymer articles (inner liner, intermediate layer or

30 layers and outer cover) in the form of a tube-formed polymer layer wherein at least one of the tube-formed polymer layers is produced according to the process defined in the claims.

35 Furthermore the invention relates to a flexible unbonded offshore pipe comprising at least one polymer layer, said



polymer layer being obtainable using the process as defined in the claims.

The flexible unbonded offshore pipe may have any shape  
5 e.g. as known from WO 00/36324 and US 6,085,799, which  
are hereby incorporated by reference. One or more of the  
tube-formed polymer layers, e.g. the inner liner,  
intermediate layer or layers and/or outer cover, may be  
10 produced using the process of the invention.

Fig. 1 is a sketch of a production line usable in the  
process of the invention.

Fig. 1 is a sketch of a production line for the  
15 production of an inner liner for an offshore pipeline. A  
carcass, i.e. a metal armouring 1, of an offshore  
pipeline is unwound from a coil 2 and passes through a  
calibrating device 3. An extrusion device 4 extrudes a  
polyethylene inner liner onto the carcass, and the  
20 extruded inner liner passes together with the carcass  
directly to a cross-linking zone 5, where it is subjected  
to a heat treatment, e.g. with infrared radiation. From  
the cross-linking zone 5, it passes onto a first cooling  
zone 6, wherein the heated polyethylene inner liner is  
25 cooled. From the first cooling zone 6, it passes onto a  
second cooling zone 7, wherein it is further cooled. From  
the second cooling zone 7, it passes through a second  
calibrating device 8 and further to a coil 9 onto which  
it is wound.

30 The present invention includes passing the extruded  
polymer material directly through a cross-linking zone.  
In the cross-linking zone, the material is subjected to  
an intensive heating, e.g. infrared radiation. In the  
35 cross-linking zone, the heating means e.g. infrared  
heaters are arranged to surround the extruded polymer

material so as to subject the polymer material to heat from all sides or angles. The extruded polymer material preferably enters the cross-linking zone immediately after extrusion or no later than 2 minutes after  
5 extrusion.

The velocity of the extrusion of the polymer material is approximately equal to the velocity of the extruded polymer passing through the cross-linking zone. A  
10 preferred velocity is between 0.2 to 2 m/minute, preferably between 0,5 and 1,0 m/minute.

From the crosshead tool, the pipe preferably passes into a first chamber, wherein it is subjected to heat from  
15 heating means, e.g. infrared heaters.

The pipe should preferably be in the first chamber for a sufficient time to initiate cross-linking of the inner liner. The necessary time can be determined by cross-  
20 linking thin samples for various periods of time. Based on this time and the knowledge of the extrusion line speed, the necessary minimum length of the first chamber can be calculated.

25 After being treated in a first cross-linking chamber, the inner liner may optionally be introduced into a second chamber, where the inner liner is cooled optionally by water cooling.

30 After being treated in a first cross-linking chamber and optionally a second cooling chamber, the inner liner may be introduced into a third chamber, where the inner liner is further cooled.

35 The third chamber may preferably be a traditional cooling chamber with water suspension or water spraying onto the

pipe containing the inner liner. Typically, tap water at ambient temperature is used or recirculating water connected to a heat exchanger. Time and thus length of the chamber should preferably be sufficient to cool down  
5 the pipe to below approximately 60°C to assure sufficient strength of the inner liner so that it may be handled by the caterpillar belts without any damage.

The total length of the cross-linking and cooling  
10 chambers should preferably for practical reasons be kept below 100 meters in length. On the other hand, the cooling sections in the prior art processes are typically several tens of meters in length. The total length of a line for prior art extrusion of large dimension flexible  
15 pipes is well above one hundred meters.

Please observe that all though the first chamber, the second chamber and the third chamber, respectively, are sometimes referred to as one chamber, these chambers each  
20 represent a treatment, which in practice may be conducted in two or more physically separated treatment chambers. Consequently, the first chamber represents a first step of the treatment of the extruded inner liner, the second chamber represents a second step of the treatment of the  
25 extruded inner liner, and the third chamber represents a third step of the treatment of the extruded inner liner.

However, according to the invention the cooling of the polymer material may optionally be effected in one step  
30 in one chamber as one cooling treatment.

One effect of cross-linking polyethylene is that the material may be used at higher operating temperatures without being deformed due to good chemical and  
35 mechanical properties. It is expected that the operating

temperature can be increased from approx. 60°C to approx. 90°C for typical offshore applications.

5 A few simple methods of characterising the cross-linking are probe penetration, hot set and the degree of cross-linking determined by decaline extraction.

10 The hot set test, as specified in IEC 811-2-1, clause 9 and as used in several electrical cable standards as e.g. VDE 0273 and IEC 502, measures the mechanical elongation (set) of a test specimen at 200°C under a specified load. The lower the value is, the higher the degree of cross-linking. If not cross-linked at all, the sample will simply flow away. It further measures a cold set after  
15 removal (a residual set). A well cross-linked sample will have essentially no cold residual set.

The degree of cross-linking is measured by decalin extraction according to the ASTM D 2765 standard  
20 prescribing a 6-hour extraction. The degree of cross-linking is simply the relative weight of unextractable material. By experience, values for cross-linked polyethylene are normally in the 75% to 80% range. The inventors' experience with new improved process is that  
25 the degree of cross-linking is often higher, in the 80 to 90% range. This method of measuring the degree of cross-linking has the disadvantage of being destructive, because it is necessary to cut out a piece of the material. Thus this method is unsuitable for quality  
30 control of the cross-linking step of inner liners.

The probe penetration test measures the relative % of penetration of a 1 mm diameter cylindrical probe into a sample of the material at a given temperature under a  
35 given load. The inventors have found suitable parameters to be a load of 300 mN for samples of 2 to 3 mm

thickness, and heating by 5°C/minute from 25° to 150°C. This method has the advantage of being non-destructive,.

5 For cross-linked polyethylene with over 70% degree of cross-linking, the penetration at 140°C is typically less than 25%. Un-cross-linked polyethylene has 100% penetration, and partially cross-linked samples give intermediate penetration values. We suggest the use of 30% as maximum penetration indicative of sufficient  
10 cross-linking, corresponding to approximately 65% degree of cross-linking.

## CLAIMS:

1. A process for the preparation of an elongated polymer article comprising the steps of shaping a polymer material by extrusion into or onto a supporting unit in an extrusion station and cross-linking said extruded polymer material, said polymer material comprising a polyethylene and a peroxide for providing a crosslinking of the polymer material, said peroxide having an activation temperature substantially above, preferably at least 5 °C above, more preferably at least 10 °C above the temperature of the polymer material during the extrusion thereof, which extrusion and cross-linking steps are carried out in an in-line process, including passing the extruded polymer material from the extruder through a cross-linking zone to activate said peroxide whereby the polymer material is cross-linked, wherein said activating is performed by applying heat in the cross-linking zone.
2. A process according to claim 1 wherein the supporting unit is a reinforcement material, preferably a reinforcement layer of a flexible unbonded offshore pipe.
3. A process according to claim 2 wherein the supporting unit is in the form of a carcass, said polymer article being an inner liner of a flexible unbonded offshore pipe and said polymer material being extruded onto the carcass.
4. A process according to claim 2 wherein the supporting unit is in the form of a pressure armour, said polymer article being an intermediate layer of a flexible unbonded offshore pipe and said polymer material being extruded onto the pressure armour.

5. A process according to claim 2 wherein the supporting unit is in the form of a tensile amour, said polymer article being an outer cover of a flexible unbonded offshore pipe and said polymer material being extruded onto the tensile amour.

6. A process according to any one of the preceding claims wherein the polymer article is an inner liner of a flexible unbonded offshore pipe, said inner liner preferably being extruded into a supporting unit, said supporting unit being in the form of a calibrating device, which calibrates the outer dimension of the pipe using vacuum onto a supporting surface.

7. A process according to any one of the preceding claims wherein the polyethylene has a density of at least  $920 \text{ g/cm}^3$ , such as above  $940 \text{ g/cm}^3$ , preferably the polyethylene has a density between  $945$  to  $955 \text{ g/cm}^3$ .

8. A process according to any one of the preceding claims wherein the polymer composition comprises at least 50 % by weight, preferably at least 70 % by weight, more preferably at least 85 % by weight of polyethylene.

9. A process according to any one of the preceding claims wherein the polymer composition comprises up to about 10 % by weight, such as up to about 5 % of fillers, preferably selected from the group consisting of pigments, heat stabilisers, process stabilisers, metal deactivators, flame retardants and reinforcement fillers, said reinforcement fillers preferably being selected from the group consisting of carbon black, glass particles, glass fibres, mineral fibres, talcum, carbonates, mica, and silicates.

10 A process according to any one of the preceding claims

wherein the polymer composition comprises up to about 40 % by weight, such as up to about 20 % or preferably up to about 10 % by weight of additional polymer(s) other than polyethylene, said additional polymer(s) preferably being  
5 selected from the group consisting of thermoplastics such as thermoplastic elastomers including block copolymer such as SEBS, SBS, SIS, TPE-polyether-amide, TPE-polyether-ester, TPE-urethanes, TPE PP/NBR, TPE-PP/EPDM, TPE-vulcanisates and TPE-PP/IIR; rubbers such as  
10 butadiene rubber, isoprene rubber, nitril rubber, styrene-butadiene rubber and urethane rubber; polyolefins such as polypropylene and polybutylene including its isomers; liquid crystal polymers; polyesters; polyacrylates; polyethers; polyurethane; thermplastic  
15 vulcanisates; and Liquid Silicone Rubber.

11. A process according to any one of the preceding claims wherein the amount of peroxide in the polymer composition is at least 0.1 % by weight of the polymer  
20 composition, such as between 0.2 and 3 % by weight of the polymer, more preferably up to about 2 % or even more preferably up to about 1.5 % by weight of the polymer composition.

25 12. A process according to any one of the preceding claims wherein the polymer composition comprises from 0.1 to 1.0 % by weight, preferably from 0.3 to 0.8 % by weight of peroxide.

30 13. A process according to any one of the preceding claims wherein the peroxide has an activation temperature above 145°C, said peroxide preferably being selected from the group consisting of butylcumylperoxide, dicumylperoxide, Trigonox 145B, hydroperoxide and  
35 butylhydroperoxide.



14. A process according to any one of the preceding claims wherein the wherein the application of heat in the cross-linking zone is applied using infrared heating, microwave heating, conventional heating, heating by hot gas and hot moistened gas, such as hot moistened air or hot steam.
15. A process according to any one of the preceding claims wherein the pressure in the cross-linking zone is raised to avoid formation of bubbles and irregularities, said pressure preferably being above 1.5 bar, more preferably above 2 bar, such as between 2.5 and 10 bar.
16. A process according to claim 1 wherein the extruded material is subjected to heat treatment in said cross-linking zone for 5 to 120 seconds, preferably for 10 to 60 seconds.
17. A process according to any one of the preceding claims wherein the extruded polymer material is subjected to a heat treatment in said cross-linking zone at a temperature above 145 °C preferably at a temperature between 150 and 200 °C.
18. A process according to any one of the preceding claims wherein the degree of cross-linking obtained is 75 to 90 %, preferably the degree of cross-linking is 80 to 85 %.
19. A process according to any one of the preceding claims wherein the extruded polymer material enters the cross-linking zone immediately after extrusion or no later than 2 minutes after extrusion.
20. A process according to any one of the preceding claims wherein the extruded material from the cross-

linking zone is cooled to ambient temperatures.

21. A process according to any one of the preceding claims wherein the supporting unit is a metallic material, preferably in the form of a reinforcing layer of an flexible unbonded offshore pipe.

22. A process according to claim 21 wherein the metallic material reflects heat applied in the cross-linking zone.

23. A process according to claim 21 wherein the supporting unit is an amour layer comprising a tape applied onto the amour, the polymer composition being extruded onto said tape, said tape having a reflecting surface reflecting the heat applied in the cross-linking zone, said reflecting surface of the tape preferably being capable of reflecting at least 50 % of the heat applied to the tape using infrared heating or microwave heating.

24. A process according to any one of the preceding claims wherein the velocity of the extrusion of the polymer material is approximately equal to the velocity of the extruded polymer passing through the cross-linking zone, said velocity preferably being between 0.2 to 2 m/minute, preferably between 0,5 and 1,0 m/minute.

25. A process according to any one of the preceding claims wherein the elongated polymer article is an inner liner, preferably an inner liner for an offshore pipe.

26. A method for the production of a flexible unbonded offshore pipe comprising one or more polymer articles in the form of a tube-formed polymer layer, one or more of said polymer layers being produced according to the process defined in any one of the claims 1-25.

27. A flexible unbonded offshore pipe comprising at least one polymer layer, said polymer layer being obtainable using the process as defined in any one of the  
5 claims 1-25.

28. A flexible unbonded offshore pipe comprising an inner liner obtainable using the process as defined in  
10 any one of the claims 1-25.

29. A flexible unbonded offshore pipe comprising an outer cover obtainable using the process as defined in any one of the claims 1-25.

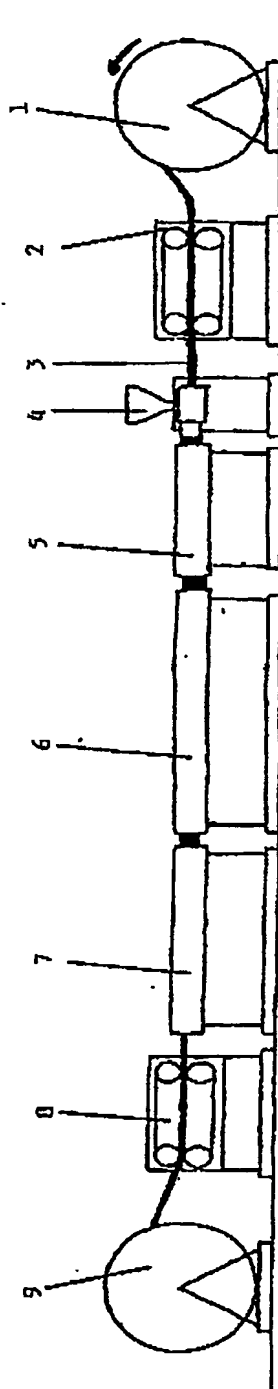
15 30. A flexible unbonded offshore pipe comprising an intermediate polymer layer obtainable using the process as defined in any one of the claims 1-25.

Patent- og  
Varemærkestyrelsen

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Modtaget

FIGURE 1



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